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A Gas Chromatographic Micromethod for Trace Determinations of Phenols

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Abstract

A gas chromatographic procedure is described for the analysis of a variety of substituted phenols from water samples. The method was designed for situations when the sample size is very limited (0.5 to 1.0 ml), such as in laboratory microcosm experiments on transport and fate of pollutants. The phenols were extracted, derivatized, and quantified by flame ionization and electron capture detection. Toluene gave a better extraction efficiency than acetone, hexane, dichloromethane, and ethylacetate, yielding essentially the same recovery from spiked well water samples as direct acetylation with acetic anhydride. Between 5 and 35 ng/ml of different phenols were detected. The heptafluorobutyryl derivatives possessed high electron capture sensitivity, ranging from 0.1 to 7.6 pg of individual phenols. The practical detection limit for phenol, chlorophenols, *p*-cresol, dimethyl-, and nitrophenols was from 0.01 to 0.20 ng/ml, with one exception, 2,4-dinitrophenol, which had low extractability and electron capture sensitivity, resulting in a detection limit of 1.6 ng/ml.

Introduction

Due to the high toxicity of low-chlorinated and non-halogenated phenols and the widespread contamination of the environment from sources such as the petrochemical and paper industries (1,2) and municipal wastes (3), these chemicals have been included on the U.S. Environmental Protection Agency (EPA) list of priority pollutants. Chlorination of drinking water may also produce chlorophenols (4), and at least one of the phenols, 2,4,6-trichlorophenol, has been shown to be carcinogenic in test animals (5). Consequently, it has become important to monitor traces of these compounds in the environment and to perform experiments on their transport and degradation in defined media.

Traces of pollutants have been isolated from water samples by solvent extraction or adsorption on XAD or similar resins and subsequently separated and quantitated by gas chromatography. Because of the high polarity and low vapour pressure of phenols (6), a derivatization step has often been used in analysis of these compounds to achieve improved chromatographic performance and, sometimes, more efficient extraction from aqueous samples. Reagents such as diazomethane (7), alpha-bromo-2,3,4,5,6-pentafluorotoluene (8), 1-fluoro-2,4-dinitrobenzene (9,10), silanizing reagents (11), heptafluorobutyrylimidazole (12), acetic anhydride (13,14), and pentafluorobenzoyl chloride (15) have been employed for this purpose.

Several methods utilizing simultaneous derivatization and extraction coupled with electron capture gas chromatography for analysis of chlorinated phenols in aqueous samples have recently been described (15-17). While these procedures appear quite effective for many analytical needs, they lack the sensitivity required when samples are limited to a very few milliliters or microliters and subpicomoles of individual phenols with varying substituents, which is often the case in laboratory studies of environmental transport and fate of pollutants.

The objective of the work described in this paper was to develop a micromethod for the GC determination of trace quantities of chloro, nitro, and methyl phenols in water samples of minute volume. Several procedures for extraction of phenols from aqueous samples by organic solvents were evaluated, and the optimal conditions to form and detect derivatives of heptafluorobutyricanhydride (HFBA) were determined. Based on this work, an optimized analytical procedure involving extraction of phenols from 0.5- to 1.0-ml aqueous samples with toluene, derivatization of extracted phenols with HFBA, and separation and quantitation of derivatives by electron capture gas chromatography was developed. The procedure was used to measure trace concentrations of phenols in a laboratory ground water microcosm.

Experimental

Apparatus

A Model 4160 gas chromatograph (Carlo Erba) was used with capillary on-column or splitless injection, and flame ionization detection (FID) or ^{63}Ni electron capture detection (ECD) with 5-msec pulse width. Chromatography was performed on either a 30-m × 0.32-mm or a 15-m × 0.25-mm methyl polysiloxane

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coated fused silica column obtained from J&W Scientific. Nitrogen was used both as carrier gas (1.8 ml/min) and make-up gas (18 ml/min for FID and 28 ml/min for ECD). The temperature of the splitless injector was 220°C, the FID was maintained at 250°C, and the ECD at 300°C. The oven was maintained at 45°C for 5 min, then programmed at 8°/min to 165°C and held there for 1 min. Sample volumes injected were 0.5 to 1.0 μl and peak areas were measured using a Model 3388 integrator equipped with an interface (both from Hewlett-Packard).

Standards and reagents

Phenol, *p*-cresol, 2,4-dimethylphenol, chlorophenols, nitrophenols, and the two internal standards, 2-fluorophenol (2-FP) and 1,6-dibromobenzene (P-DBB), were all supplied by Chem Service, Inc. Toluene was from Burdick and Jackson Labs, Inc. and Mallinckrodt, Inc., and was distilled twice prior to use. Hexane, acetone, dichloromethane, ethyl acetate, hydrochloric acid, and sodium hydroxide were from Mallinckrodt. Acetic anhydride was supplied by Supelco, Inc. and HFBA was from Pierce Chemical Co.

Sample preparation

Preparation for flame ionization detection. Phenols were dissolved in 95% ethanol to give a concentration of 0.05 mmol. A 100-μl aliquot of the ethanol standard was diluted in 10 ml filter sterilized well water in a volumetric flask. The solution was stirred for one day with a magnetic bar to ensure complete mixing. A 1-ml sample was added to a 4-ml vial with an autopipet, 10 μl 2-fluorophenol added, and the sample acidified with 6*M* HCl to pH 3.0 or buffered with 2 drops of $NaHCO_3$ (15g/100 ml) to pH 8.5. One milliliter of hexane, hexane/acetone (1:1), ethyl acetate, dichloromethane, or toluene was added. The mixture was shaken for 20 min on a wrist-action shaker. The top layer was removed by a Pasteur pipet to a 2-ml vial. The extraction was repeated once and the resulting extract kept in a separate vial until analyzed.

Extraction of the parent molecules was compared with extraction of the acetates. 2-Fluorophenol (10 μl) was added to a 1-ml sample and pH was adjusted either to 3.0 with HCl or to 8.5 with $NaHCO_3$. The sample was heated with 5 μl acetic anhydride and 1 ml ethyl acetate or toluene for 5 min at 60°C.

The effect on extraction efficiency of a larger alkyl group on the ester was studied from the reaction of 5 μl butyric anhydride with the phenols in water solution and subsequent extraction with ethyl acetate. The effect of extraction ratio was studied for underivatized compounds extracted by toluene at water-to-toluene ratios of 1:1, 20:1, and 100:1. For the latter ratio, extractions were conducted in glass tubes with an i.d. of 4 mm to permit recovery of the added 10 μl of toluene.

Preparation for electron capture detection. Toluene (500 or 100 μl) was added to a 500-1 well water sample spiked with phenols at pH 3.0 or 8.5. The concentrations of phenols were from 100 to 0.50 ng/ml. The vial was shaken vigorously and manually for 30 sec and then on a wrist-action shaker for 15 min. The toluene layer was transferred by a Pasteur pipet to a 2-ml vial and 10 μl HFBA added. The vial was shaken vigorously for 30 sec and then placed on a water bath at 60°C for 5 min. The sample was cooled in a freezer for 10 min and excess reagent hydrolyzed by adding 100 μl 1*M* NaOH, shaking the sample for 30 sec, and then centrifuging for 10 min. The toluene layer was transferred to a 2-ml vial, and the second internal standard, 1,6-dibromobenzene, added just prior to analysis.

Results and Discussion

Toluene was found to be the most efficient extraction solvent for phenols, followed by acetone/hexane, ethyl acetate, and dichloromethane (Table I). The favourable distribution coefficient for phenols between toluene and water probably arises from the mobile π-electrons, which may induce dipole attractions with the phenols. The second most efficient solvent, acetone/hexane, introduces a water soluble organic compound, which enhances the polarity of the hexane phase, thus improving extraction efficiency. Acylation with acetic or butyric anhydride followed by extraction with ethyl acetate was comparable to toluene in efficiency. The conversion of the phenols to their corresponding esters prior to extraction improved their solubility in the organic solvent and produced better GC peak symmetry than the underivatized compounds.

The phenolate ion present in the alkaline solution was readi-

Table I. Percentage Recovery of Phenols*

Compound	Spiked amount (ng)	Extraction solvents** A $\bar{X}$	A CV	B $\bar{X}$	B CV	C $\bar{X}$	C CV	D $\bar{X}$	D CV	E $\bar{X}$	E CV	F $\bar{X}$	F CV	G $\bar{X}$	G CV	H $\bar{X}$	H CV	I $\bar{X}$	I CV	J $\bar{X}$	J CV	K_{ow}
Phenol	93.1	45.9	4.2	52.5	5.6	62.3	4.6	57.0	3.1	65.5	4.4	82.7	2.3	85.4	7.3	74.0	6.0	95.0	3.6	78.2	7.2	30
2-Chlorophenol	77.4	50.2	8.5	45.5	3.4	60.7	3.5	50.4	4.0	62.6	6.3	70.1	1.7	68.3	4.5	73.5	8.3	96.4	2.8	66.4	4.3	151
2,4-Dichlorophenol	126.2	64.8	3.6	40.8	5.1	55.1	5.5	66.5	3.7	70.9	5.5	82.0	3.4	88.0	5.1	73.5	4.7	96.7	4.1	70.9	4.6	790
2,4,6-Trichlorophenol	86.2	82.9	10.4	n.d.	—	67.8	8.3	66.2	4.3	98.7	8.8	102.0	2.8	99.3	3.4	53.1	6.5	99.5	4.0	75.1	5.8	4100
p-Cresol	76.2	89.3	5.9	81.1	6.2	64.4	4.7	75.8	5.4	80.4	6.0	104.5	0.6	92.8	6.0	75.0	3.4	97.5	2.8	69.3	5.2	—
2,4-Dimethylphenol	77.6	77.9	4.8	83.2	5.7	73.6	6.9	81.1	6.0	84.4	9.4	100.0	1.0	90.6	2.3	86.6	6.2	82.2	3.3	78.6	4.7	630
2-Nitrophenol	83.3	68.8	8.7	n.d.	—	56.4	8.3	56.2	7.3	73.8	7.9	78.9	0.8	81.4	7.5	85.5	4.6	83.2	4.4	73.9	6.0	56
4-Nitrophenol	80.6	55.2	6.4	n.d.	—	47.3	9.7	38.9	6.8	40.0	11.4	42.9	2.6	96.3	6.3	84.2	5.0	88.0	4.6	84.7	5.4	93
2,4-Dinitrophenol	86.6	30.1	12.1	n.d.	—	n.d.	—	n.d.	—	25.3	6.2	41.7	3.1	48.5	8.4	38.9	4.8	29.3	5.1	66.5	6.6	100

*From a spiked 1-ml sample of well water, subject to GC analysis by flame ionization detection after different extraction and derivatization procedures. CV = coefficient of variation (%), $n = 6$, K_{ow} = octanol-water partition coefficient, n.d. = not detectable.

**Solvent identification: A = acetone + hexane (pH 3.0); B = acetone + hexane (pH 8.5); C = dichloromethane (pH 3.0); D = ethyl acetate (pH 3.0); E = toluene (pH 3.0); F = toluene (pH 8.5); G = triethylamine + toluene; H = acetic anhydride + ethyl acetate (pH 3.0); I = acetic anhydride + ethyl acetate (pH 8.5); J = butyric anhydride + ethyl acetate (pH 8.5).

ly derivatized and extracted by ethyl acetate and toluene, whereas the undissociated form was more efficiently extracted by acetone/hexane. The requirement for a phenolate ion for successful derivatization has been emphasized by several authors (14-16), and the optimal compromise pH for formation of chlorinated phenolate ions has been estimated to be in the range between 9 and 10. The acetylation yield is reportedly not influenced by the buffer solution, whether carbonate, bicarbonate, or hydrogen phosphate (16). The yields here, however, were considerably lower with the phosphate buffer compared with the bicarbonate buffer.

Extraction efficiency was essentially the same at extraction ratios of 1:1, 20:1, and 100:1 (Table II). Probably as a consequence of the low volume of toluene (10 µl) the highest extraction ratio gave an increased variability. A lower yield would be expected at higher extraction ratios as predicted from Nernst distribution law (18) and has been emphasized for chlorinated phenols (16).

The nature of substituents on the parent phenol ring had a major influence on extraction efficiency. As a general rule, compounds dominated by strongly hydrogen binding groups, such as OH and NO_2, remained associated with water to a certain extent, while compounds characterized by several methyl or chlorine substituents were more easily extracted from the water.

The structural differences were also reflected in the octanol-water partition coefficients (K_{ow}, Table I). The parent compound, phenol, and the nitrophenols have the lowest K_{ow}, indicating their low affinity for the organic solvent, and were generally poorly extracted by all solvents. Each chlorine added to the phenyl molecule increases K_{ow} by a factor of 5, making 2,4,6-trichlorophenol the most organophilic of the compounds. This graduated affinity of the chlorophenols for the organic phase is less clearly expressed in the differences in extraction efficiencies for the solvents used.

The variation in extraction efficiency of the phenols influenced the practical detection limit of the method. With phenyl acetates extracted by ethyl acetate the FID response limit was 0.5 ng for the nitrophenols, 2,4-dimethylphenol, and 2,4,6-trichlorophenol. Although the last two compounds were efficiently extracted, the response factor on FID was comparatively low, or alternatively, the adsorption to the column matrix high. The FID responded to 0.3 ng of 2,4-dichlorophenol and to 0.1 ng of the rest of the phenols. This resulted in detection limits for the phenols in the range of 5 to 35 ng/ml.

Table II. Effect of Extraction Ratio on Extraction Efficiency (%) of Phenols*

Compound	Spiked amount (ng)	Ratio of water:toluene 1:1	20:1	100:1
Phenol	93.1	65.5	65.8	61.1
2-Chlorophenol	77.4	62.6	61.7	58.0
2,4-Dichlorophenol	126.2	70.9	71.6	71.4
2,4,6-Trichlorophenol	86.2	98.7	97.3	98.2
p-Cresol	76.2	80.4	78.1	79.6
2,4-Dimethylphenol	77.6	84.4	86.0	85.1
2-Nitrophenol	83.3	73.8	72.7	73.8
4-Nitrophenol	80.6	40.0	42.6	41.5
2,4-Dinitrophenol	86.6	25.2	28.1	27.9

*From a spiked 1-ml sample of well water using toluene as extractant at pH 3.0. The average of six replicates is shown.

The yield of the heptafluorobutyryl derivatives from an acidified water sample was higher, generally by a factor of 2 to 3, compared with an alkaline water sample (Table III), indicating that acylation with HFBA proceeded far more rapidly on the undissociated compounds than on the phenolate ions. Increasing the reaction temperature from ambient to 60°C improved the yield and especially the replicability. Traces of unreacted HFBA in the injected samples increased the standard variation, but treatment with 1*M* NaOH provided efficient clean-up.

The electron capture sensitivity varied, with one exception, by a factor of 30 between the least and most sensitive compounds (Table IV). The exception was 2,4-dinitrophenol, which was by far the least sensitive compound. Interestingly, 2-nitrophenol and 4-nitrophenol were most sensitive to detection, suggesting that the acylation of 2,4-dinitrophenol may be hampered by unfavourable electron distribution in the molecule. For the other compounds, 0.1 to 3.3 pg of derivative injected gave a detectable peak in a chromatogram. This is about five times more sensitive than corresponding 2,4-dinitrophenyl ethers (10). The sensitivity of the ECD in itself to the HFBA derivatives was probably twice as high as in Table IV. When small amounts of compounds were injected, the response on the detector became much lower than predicted from the dose-response regres-

Table III. Influence of pH of the Water Sample on the Yield of Phenylheptafluorobutyrate*

Compound	Peak area phenols/peak area ISTD at pH 8.5 pH 3.0	pH 8.5
1-Fluorophenol (ISTD)	2.08	1.00
Phenol	1.01	0.47
2-Chlorophenol	0.83	0.32
2,4-Dichlorophenol	1.09	0.60
2,4,6-Trichlorophenol	0.53	0.19
p-Cresol	1.60	0.70
2,4-Dimethylphenol	2.45	1.59
2-Nitrophenol	0.41	0.04
4-Nitrophenol	0.23	0.12
2,4-Dinitrophenol	0.06	0.02

*All peak areas are divided by the peak area for the internal standard (1-fluorophenol) at pH 8.5, which is taken to be equal to 1. The average of six replicates is shown.

Table IV. Electron Capture Detector Sensitivity (ES), Coefficient of Variation, and Practical Detection Limit for HFBA Derivatives of Phenols

Compound	ES* (pg)	CV (%)	Detection limit** (ng/ml)
Phenol	2.3	11.0	0.19
2-Chlorophenol	2.6	6.5	0.22
2,4-Dichlorophenol	0.7	6.2	0.22
2,4,6-Trichlorophenol	1.1	19.3	0.07
p-Cresol	2.6	6.7	0.18
2,4-Dimethylphenol	3.3	12.7	0.22
2-Nitrophenol	0.2	8.2	0.01
4-Nitrophenol	0.1	12.0	0.01
2,4-Dinitrophenol	7.6	7.9	1.62

*Expressed as the amount of derivative injected to produce a peak five times larger than the baseline noise level. This limit was sufficient to account for mean values and standard deviation of noise peaks plus the desired degree of confidence, 90 to 95% (equivalent to a multiplier of 3 in a t-distribution).

**The practical detection limit is calculated by multiplying the ES value by the extraction volume, 50 µl, for a water-to-toluene extraction ratio of 20:1, by the extraction efficiency of toluene at pH 3.0 and by the CV for the method.

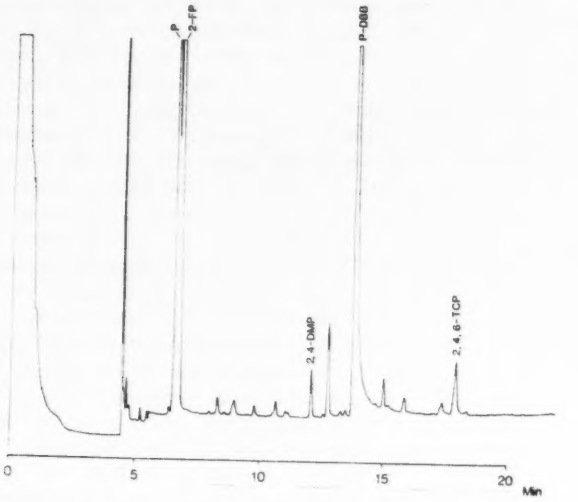

Figure 1. Gas chromatogram of an interstitial pore water sample (1 ml) from a ground water microcosm. Phenols were supplied in sterilized well water at a concentration of 10 μg/l, extracted by toluene and derivatized by HFBA. The peaks represent 89 pg (P), 7 pg (2,4-DMP) and 4 pg (2,4,6-TCP). P=phenol, 2-FP=2-fluorophenol, 2,4-DMP=2,4-dimethylphenol, P-DBB=1,6-dibromobenzene, 2,4,6-TCP=2,4,6-trichlorophenol.

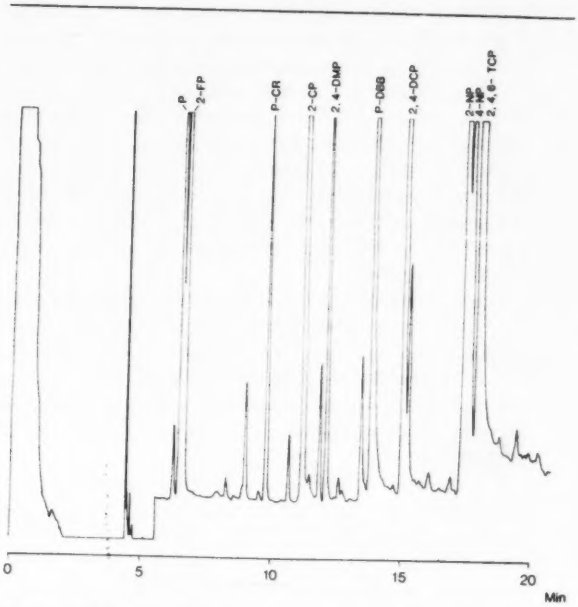

Figure 2. Gas chromatogram of a 1-ml water sample collected at the effluent of a saturated, anaerobic soil column, supplied with filter sterilized well water fortified with nine phenols, each at a concentration of 1 mg/l. The peaks represent from 34 (*p*-cresol) to 427 pg (2,4,6-TCP). P=phenol, 2-FP=2-fluorophenol, P-CR=*p*-cresol, 2-CP=2-chlorophenol, 2,4-DMP=2,4-dimethylphenol, P-DBB=1,6-dibromobenzene, 2,4-DCP=2,4-dichlorophenol, 2-NP=2-nitrophenol, 4-NP=4-nitrophenol, 2,4,6-TCP=2,4,6-trichlorophenol.

sion, probably due to extensive adsorption in the analytical system. This suggests that the detector was not the limiting sensitivity factor for the GC determination, but rather the sorptive interactions between derivative and e.g., the column coating polymer. The practical detection limit was determined from 0.5- to 1.0-ml well water samples and, except for 2,4-dinitrophenol, a concentration of 0.01 to 0.2 ng/ml of individual compounds is required for a quantitative analysis. For comparison, large water samples, 100 to 1000 ml, would have to contain between 0.2 and 5 ng/l of phenols for detection, which is slightly lower than the limit of detection for chlorophenols by direct acylation of large water samples (16,17).

The method was used to determine the concentration of phenols in ground water microcosm, designed to elucidate the pattern of transport and fate of pollutants (19). The microcosm was essentially 4- × 20-cm glass columns, aseptically filled with undisturbed soil cores and operated with a water flow rate of 2 cm/day. The well water supplying the soil at this flow rate was spiked with phenols at a concentration of 1 mg/l or 10 μg/l, and residues of phenols were determined in 1-ml samples of interstitial pore water at different distances along the soil core. Loss of the original concentration of individual phenols due to sorption and degradation by a factor of 100 (from 10 to 0.1 ng/ml) was detectable. The gas chromatograms of phenols from a saturated soil microcosm are illustrated in Figure 1 for a supply of 10 μg/l and in Figure 2 for 1 mg/l.

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